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Base stable quaternary ammonium ionic liquids

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Abstract

Ionic liquids with the bis(2-ethylhexyl)dimethylammonium cation, $[BEDMA]^+$, were prepared by a halide-free route starting from the readily available secondary amine bis(2-ethylhexyl)amine. The following anions were considered: chloride, bromide, iodide, nitrate, hydrogensulphate, dihydrogenphosphate, formate, acetate, propionate, trifluoroacetate, methyl sulphate, methanesulphonate, tosylate, isonicotinate, nicotinate and picolinate. Several of the compounds are room-temperature ionic liquids, albeit with a high viscosity. All ionic liquids are soluble in water. The ionic liquids are very stable in strongly alkaline medium. No signs of decomposition could be observed by contact of the chloride ionic liquid with 50 wt% sodium hydroxide, even after prolonged heating at 80 °C. The high stability against strong bases is attributed to the branched structure of the quaternary ammonium cation, which blocks the Hofmann elimination reaction.

Introduction

Ionic liquids are solvents that consist entirely of ions, and they have usual properties such as a negligible vapour pressure, a high thermal stability, a wide electrochemical window and an intrinsic electric conductivity.[1-4] They are also excellent solvents for many classes of inorganic and organic compounds. Ionic liquids find wide applications, including solvent for catalytic reactions,[5] electrolytes for electrodeposition of reactive metals,[6-9] electrolytes for Li-ion batteries[10,11] and dye-sensitized solar cells,[12] as engineering fluids,[13,14] solvents for liquid-liquid extraction processes,[15-18] and for applications in hydrometallurgy.[19] Several ionic liquids are being used on an industrial scale.[20] Most ionic liquids are very stable against strong oxidants and reductants, as well as against strong acids, but they often have a remarkably poor resistance against strong bases.[21] Imidazolium ionic liquids are the most intensively studied class of ionic liquids, but they are not inert in alkaline medium.[22] The C(2) proton of the 1,3-dialkylimidazolium cation is quite acidic and can be exchanged under mild conditions.[23,24] Deprotonation of this acidic proton results in the formation of carbenes, and hence in the loss of the ionic character of the imidazolium ring. It is even possible to replace all hydrogen atoms on the imidazolium ring by deuterium atoms in the presence of bases.[25] Efforts have been made to avoid this unwanted deprotonation by incorporating a methyl or isopropyl group in the C(2) position of the 1,3-dialkylimidazolium ionic liquids.[26-28] However it has been reported that C(2) methyl groups of these cations will also undergo deprotonation under mild conditions.[23] Jurcik and Wilhelm synthesized a new class of ionic liquids having a phenyl substituent on the C(2) carbon position of the imidazolium ring.[29] They successfully used these ionic liquids as a reaction medium for the Baylis–Hillman reaction between methyl acrylate and a variety of aromatic aldehydes, with DABCO or quinuclidinol as the base. They also showed that these ionic liquids could be used as a solvent for reactions involving Grignard reagents. Stevens and coworkers found that peralkylated imidazolium ionic liquids

are stable against organolithium reagents.[30] Upon quenching of the reaction mixtures with D_2O, no deuterium exchange could be observed. *N*-Alkyl pyridinium ionic liquids with an ether functionality have been used as solvents for Grignard reactions.[31] Clyburne and coworkers reported that phosphonium-based ionic liquids such as tetradecyl(trihexyl)phosphonium chloride, bromide and bis(trifluoromethylsulfonyl)imide are very stable under alkaline conditions.[32,33] They also showed that Grignard reagents were stable in these ionic liquids, even after one month.[34] Quaternary phosphonium salts can be hydrolyzed in alkaline aqueous medium to a phosphine oxide and an alkane, but an organic solvent is required to accelerate the reaction.[35] Quaternary ammonium salts will undergo Hofmann degradation in the presence of strong bases, leading to the formation of an alkene and a tertiary amine.[36,37] This elimination reaction requires the presence of a β-hydrogen atom on the quaternary ammonium salt. Base stable ionic liquids could be useful as solvents for organic reactions with strongly basic reagents such as Grignard reagents or organolithium compounds. These ionic liquids could also be applied as extractants for removal of metal ions from alkaline aqueous solutions by solvent extraction.[38]

In this paper, we present new base stable ammonium ionic liquids with the bis(2-ethylhexyl)dimethylammonium cation, $[BEDMA]^+$, and with a variety of anions. All the new ionic liquids are fluorine-free (with the exception of the trifluoroacetate salt) and soluble in water.

Experimental

General information

Elemental analyses (carbon, hydrogen, nitrogen) were carried out on a CE Instruments EA-1110 elemental analyzer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz for ^{1}H and at 75.5 MHz for ^{13}C). The water content of the ionic liquids was determined by a coulometric Karl Fischer titrator (Mettler Toledo coulometric Karl Fischer titrator, model DL39).The density was measured by a pycnometer. The viscosity of the ionic liquids was determined with a Brookfield DV-II + Pro Cone/plate set-up viscometer, with a thermostatted sample cell that is being purged with dry nitrogen gas. Differential scanning calorimetry (DSC) measurements were made on a Mettler-Toledo DSC822e module, at a scan rate of 10 °C min^{-1} in a helium atmosphere. Chemicals were purchased from Acros Organics (Geel, Belgium) or from Sigma-Aldrich (Bornem, Belgium). All chemicals were used as received, without further purification.

Syntheses

Bis(2-ethylhexyl)dimethylammonium methyl sulphate, [BEDMA][CH_3SO_4]

To a suspension of potassium carbonate (45.79 g, 331.13 mmol) in acetonitrile (250 mL), bis(2-ethylhexyl)amine (20 g, 82.82 mmol) was added, followed by dimethyl sulphate (20.89 g, 165.65 mmol). The reaction mixture was refluxed for 48 hours. Potassium carbonate was removed by filtration and the solvent removed *in vacuo* to yield bis(2-ethylhexyl)dimethylammonium methyl sulphate as a pale yellow liquid. Yield: (26.84 g, 85 %).^{1}H NMR (300 MHz, D_2O): δ= 0.85 (m, 12 H), 1.25 (m, 16H), 1.81(s, 2H), 3.02 (s, 6H), 3.20 (m, 4H), 3.66 (s, 3H). ^{13}C NMR (75 MHz, D_2O): δ= 8.72, 12.45, 21.33, 24.97, 26.86,

31.53, 32.48, 48.83, 54.54, 70.19. Elemental analysis: Found: C, 59.60; H, 11.24; N, 3.52. $C_{19}H_{43}NO_4S$ requires C, 59.80; H, 11.36; N, 3.67%.

Bis(2-ethylhexyl)dimethylammonium 4-*tert*-butylphenolate, [BEDMA][4-tBuPhen]

To a solution of bis(2-ethylhexyl)dimethylammonium methyl sulphate (15 g, 39.34 mmol) in water (100 mL) sodium-4-*tert*-butylphenolate (6.77 g, 39.34 mmol) was added, followed by dichloromethane (200 mL). The mixture was vigorously stirred at room temperature for five hours. The organic layer was separated and evaporated *in vacuo* to give bis(2-ethylhexyl)dimethylammonium 4-*tert*-butylphenolate as a highly viscous liquid. Yield: (13.20 g, 80 %).^{1}H NMR (300 MHz, DMSO[D_6]): δ = 0.85 (m, 12H), 1.30 (m, 25 H), 1.41(m, 2H), 3.01(s, 6H), 3.19 (m, 4H), 7.08 (d, 2H, 8.74 Hz), 7.15 (d, 2H, 8.74 Hz).^{13}C NMR (75 MHz, DMSO[D_6]): δ = 10.07, 13.89, 22.34, 25.71, 27.58, 31.24, 32.45, 33.55, 52.78, 68.92, 114;68, 125.78, 140.55, 155.12. Elemental analysis: Found: C, 72.88; H, 10.41; N, 4.94. $C_{28}H_{53}NO$ requires C, 72.94; H, 10.62; N, 5.00%.

Bis(2-ethylhexyl)dimethylammonium acetate, [BEDMA][CH_3COO] (= general procedure)

An aqueous solution (250 mL) of glacial acetic acid (6.43 g, 107.21 mmol) was added to bis(2-ethylhexyl)dimethylammonium 4-*tert*-butylphenolate (15 g, 35.74 mmol) in toluene (50 mL). The reaction mixture was stirred vigorously at room temperature for half an hour. The aqueous layer was separated and evaporated *in vacuo* to give bis(2-ethylhexyl)dimethylammonium acetate as a colourless liquid. Yield: (11.42 g, 97 %). ^{1}H NMR (300 MHz, D_2O): δ = 0.85 (m, 12H), 1.28 (m, 16H), 1.88 (s, 3H), 1.92 (m, 2H), 2.92 (s, 6H), 3.06 (m, 4H). ^{13}C NMR (75 MHz, D_2O): δ = 9.74, 13.54, 21. 68, 22.34, 25.65, 27.82,

32.34, 33.32, 50.38, 69.66, 178.77. Elemental analysis: Found: C, 61.13; H, 12.35; N, 3.54. $C_{20}H_{43}NO_2 \cdot 3.5H_2O$ requires C, 61.34; H, 12.61; N, 3.57%.

Bis(2-ethylhexyl)dimethylammonium trifluoroacetate, [BEDMA][CF_3COO]

Bis(2-ethylhexyl)dimethylammonium trifluoroacetate was prepared by the general procedure described for [BEDMA][CH_3COO] from bis(2-ethylhexyl)dimethylammonium 4-*tert*-butylphenolate (15 g, 35.74 mmol**)** and trifluoroacetic acid (6.11 g, 53.61 mmol), to give a colourless liquid .Yield: (11.10 g, 81 %).^{1}H NMR (300 MHz, D_2O): δ = 0.85 (m, 12H), 1.29 (m, 16H), 1.92 (m, 2H), 3.00 (s, 6H), 3.20 (m, 4H).^{13}C NMR (75 MHz, D_2O): δ = 9.74, 13.54, 22.34, 25.65, 27.82, 32.34, 33.32, 50.38, 69.66, 117. 98(q), 169.32(q). Elemental analysis: Found: C, 59.90; H, 10.67; N, 3.37. $C_{20}H_{40}F_3NO_2 \cdot H_2O$ requires C, 59.82; H, 10.54; N, 3.49%.

Bis(2-ethylhexyl)dimethylammonium formate, [BEDMA][HCOO]

Bis(2-ethylhexyl)dimethylammonium formate was prepared by the general procedure described for [BEDMA][CH_3COO] from bis(2-ethylhexyl)dimethylammonium 4-*tert*-butylphenolate (15 g, 35.74 mmol**)** and formic acid (8.22 g, 178.70 mmol), to give a colourless liquid .Yield: (10.48 g, 93 %). ^{1}H NMR (300 MHz, D_2O): δ = 0.87 (m, 12H), 1.31 (m, 16 H), 1.89 (m, 2H), 3.05 (s, 6H), 3.22 (m, 4H), 6.31(s, 1H). ^{13}C NMR (75 MHz, D_2O): δ = 9.11, 12.84, 21.71, 25.37, 27.24, 31.90, 32.89, 49.32, 69.81, 169.08. Elemental analysis: Found: C, 60.32; H, 12.64; N, 3.71. $C_{19}H_{41}NO_2 \cdot 3.5\ H_2O$ requires C, 60.27; H, 12.79; N, 3.69 %.

Bis(2-ethylhexyl)dimethylammonium propionate, [BEDMA][CH_3CH_2COO]

Bis(2-ethylhexyl)dimethylammonium propionate was prepared by the general procedure described for [BEDMA][CH_3COO] from bis(2-ethylhexyl)dimethylammonium 4-*tert*-

butylphenolate (15 g, 35.74 mmol**)** and propionic acid (3.97 g, 53.61 mmol), to give a colourless liquid .Yield: (10.80 g, 88 %). ^{1}H NMR (300 MHz, D_2O): δ = 0**.**79 (m, 12H), 0.93 (t, 3H, 7.64Hz), 1.21 (m, 16H), 1.90 (m, 2H), 2.12 (m, 2H), 2.95 (s, 6H), 3.09 (m, 4H). ^{13}C NMR (75 MHz, D_2O): δ = 9.49, 9.65, 22.14, 25.80, 27.67, 29.71, 32.34, 33.30, 49.70, 70.25, 183.46. Elemental analysis: Found: C, 66.53; H, 13.23; N, 3.61. $C_{21}H_{45}NO_2{\cdot}2H_2O$ requires C, 66.44; H, 13.01; N, 3.69%.

Bis(2-ethylhexyl)dimethylammonium methanesulphonate, [BEDMA][CH_3SO_3]

Bis(2-ethylhexyl)dimethylammonium methanesulphonate was prepared by the general procedure described for [BEDMA][CH_3COO] from bis(2-ethylhexyl)dimethylammonium 4-*tert*-butylphenolate (15 g, 35.74 mmol**)** and methanesulphonic acid (3.09 g, 32.17 mmol), to give a colourless liquid. Yield: (11.23 g, 86 %). ^{1}H NMR (300 MHz, D_2O): δ = 0.91 (m, 12 H), 1.31 (m, 16H), 1.50 (m, 2H), 2.78 (s, 3H), 3.02 (s, 6H), 3.20 (s, 4H). ^{13}C NMR (75 MHz, D_2O): δ = 9.54, 13.24, 22.10, 25.76, 27.64, 31, 17, 32.30, 38.39, 49.56, 70.19.Elemental analysis: Found: C, 56.60; H, 11.85; N, 3.42. $C_{19}H_{43}NO_3S{\cdot}2H_2O$ requires C. 56.82; H, 11.79; N, 3.49%.

Bis(2-ethylhexyl)dimethylammonium tosylate, [BEDMA][TsO]

Bis(2-ethylhexyl)dimethylammonium tosylate was prepared by the general procedure described for [BEDMA][CH_3COO] from bis(2-ethylhexyl)dimethylammonium 4-*tert*-butylphenolate (15 g, 35.74 mmol**)** and 4-methylbenzenesulfonic acid (5.84 g, 33.95 mmol), to give a colourless solid. Yield: (12.63 g, 80%). mp: 78 ºC. ^{1}H NMR (300 MHz, D_2O): δ = 0.80 (m, 12H), 1.38 (m, 16H), 1.42 (m, 2H), 2.31 (s, 3H), 2.94 (s, 6H), 3.12 (m, 4H), 7.27 (d, 2H), 7.61 (d, 2H). ^{13}C NMR (75 MHz, D_2O): δ = 9.45, 13.19, 20.37, 22.06, 25.68, 27.58,

32.24, 33.20, 70.15, 125.24, 129.32, 139.32, 142.33. Elemental analysis: Found: C, 62.21; H, 18.31; N, 3.00. C_{25} $H_{47}NO_3S \cdot 2H_2O$ requires C, 62.29; H, 18.19; N, 2.91%.

Bis(2-ethylhexyl)dimethylammonium chloride, [BEDMA][Cl]

Bis(2-ethylhexyl)dimethylammonium chloride was prepared by the general procedure described for [BEDMA][CH_3COO] from bis(2-ethylhexyl)dimethylammonium 4-*tert*-butylphenolate (15 g, 35.74 mmol**)** and hydrochloric acid (37 % solution, 3.52 mL, 1.30 g, 35.74 mmol), to give a colourless solid. Yield: (9.18 g, 84%). mp: 84 ºC. ^{1}H NMR (300 MHz, D_2O): δ = 0.87 (m, 12H), 1.35 (m, 16H), 1.45 (m, 2H), 2.9 (s, 6H), 3.15 (m, 4H). ^{13}C NMR (75 MHz, D_2O): δ = 9.74, 13.54, 22.34, 25.65, 27.82, 32.34, 33.32, 50.38, 69.66. Elemental analysis: Found: C, 58.74; 12.76; N, 3.81. $C_{18}H_{40}ClN \cdot 3.5H_2O$ requires C, 58.58; H, 12.83; N, 3.79%.

Bis(2-ethylhexyl)dimethylammonium bromide, [BEDMA][Br]

Bis(2-ethylhexyl)dimethylammonium bromide was prepared by the general procedure described for [BEDMA][CH_3COO] from bis(2-ethylhexyl)dimethylammonium 4-*tert*-butylphenolate (15 g, 35.74 mmol**)** and hydrobromic acid (48 % solution, 6.02 mL, 2.89 g, 35.74 mmol), to give a colourless solid .Yield: (10.14 g, 81%). mp: 90 ºC. ^{1}H NMR (300 MHz, D_2O): δ = 0.85 (m, 12H), 1.32 (m, 16H), 1.45 (m, 2H), 2.93 (s, 6H), 3.14 (m, 4H). ^{13}C NMR (75 MHz, D_2O): δ = 9.74, 13.54, 22.34, 25.65, 27.82, 32.34, 33.32, 50.38, 69.66. Elemental analysis: Found: C, 58.55; H, 11.33; N, 3.80. $C_{18}H_{40}BrN \cdot H_2O$ requires C, 58.67; H, 11.49; N, 3.80%.

Bis(2-ethylhexyl)dimethylammonium iodide, [BEDMA][I]

Bis(2-ethylhexyl)dimethylammonium iodide was prepared by the general procedure described for [BEDMA][CH_3COO] from bis(2-ethylhexyl)dimethylammonium 4-*tert*-butylphenolate (15 g, 35.74 mmol**)** and hydrogen iodide (57 % solution, 8.02 mL, 4.57 g, 35.74 mmol), to give a colourless solid. Yield: (11.36 g, 80%). mp: 73 ºC. ^{1}H NMR (300 MHz, D_2O): δ = 0.80 (m, 12H), 1.22 (m, 16H), 1.42 (m, 2H), 2.96 (s, 6H), 3.13 (m, 4H). ^{13}C NMR (75 MHz, D_2O): δ = 9.73, 13.54, 22.31, 25.60, 27.82, 32.34, 33.32, 50.38, 69.66. Elemental analysis: Found C, 40.12; H, 9.50; N, 2.40. $C_{18}H_{40}IN$ requires: C, 40.18; H, 9.05; N, 2.47%.

Bis(2-ethylhexyl)dimethylammonium hydrogensulfate, [BEDMA][HSO_4]

Bis(2-ethylhexyl)dimethylammonium hydrogensulfate was prepared by the general procedure described for [BEDMA][CH_3COO] from bis(2-ethylhexyl)dimethylammonium 4-*tert*-butylphenolate (15 g, 35.74 mmol**)** and sulphuric acid (95 % solution, 3.68 mL, 3.50 g, 35.74 mmol), to give a colourless liquid .Yield: (10.64 g, 81%). ^{1}H NMR (300 MHz, D_2O): δ = 0.89 (m, 12H), 1.30 (m, 16H), 1.43 (m, 2H), 3.00 (s, 6H), 3.20 (m, 4H). ^{13}C NMR (75 MHz, D_2O): δ = 9.45, 13.26, 22.11, 25.69, 27.63, 32.25, 33.23, 49.99, 69.90. Elemental analysis: Found: C, 51.22; H, 11.35; N, 3.18. $C_{18}H_{41}NO_4S{\cdot}3H_2O$ requires C, 51.28; H, 11.24; N, 3.32%.

Bis(2-ethylhexyl)dimethylammonium dihydrogenphosphate, [BEDMA][H_2PO_4]

Bis(2-ethylhexyl)dimethylammonium dihydrogenphosphate was prepared by the general procedure described for [BEDMA][CH_3COO] from bis(2-ethylhexyl)dimethylammonium 4-*tert*-butylphenolate (15 g, 35.74 mmol**)** and phosphoric acid (85 % solution, 4.12 mL, 3.50 g, 35.74 mmol), to give a colourless liquid. Yield: (10.50 g, 80%). ^{1}H NMR (300 MHz, D_2O): δ = 0.86 (m, 12H), 1.28 (m, 16H), 1.45 (m, 2H), 3.02 (s, 6H), 3.20 (m, 4H). ^{13}C NMR (75 MHz, D_2O): δ = 9.45, 13.29, 22.11, 25.69, 27.63, 32.23, 33.23, 49.99, 69.93. Elemental analysis:

Found: C, 53. 46; H, 11.37; N, 3.60. $C_{18}H_{42}NO_4P{\cdot}2H_2O$ requires C: 53.57, H: 11.49, N: 3.47%.

Bis(2-ethylhexyl)dimethylammonium nitrate, [BEDMA][NO_3]

Bis(2-ethylhexyl)dimethylammonium nitrate was prepared by the general procedure described for [BEDMA][CH_3COO] from bis(2-ethylhexyl)dimethylammonium 4-tert-butylphenolate (15 g, 35.74 mmol) and nitric acid (65 % solution, 3.46 mL, 2.25 g, 35.74 mmol), to give a colourless liquid. Yield: (10.10 g, 85%). ^{1}H NMR (300 MHz, D_2O): δ = 0.88 (m, 12H), 1.25 (m, 16H), 1.45 (m, 2H), 3.02 (s, 6H), 3.20 (m, 4H). ^{13}C NMR (75 MHz, D_2O): δ = 9.45, 13.29, 22.11, 25.69, 27.63, 32.23, 33.23, 49.99, 69.93. Elemental analysis: Found: C, 58.52; H, 12.10; N, 7.57. $C_{18}H_{40}N_2O_3{\cdot}2H_2O$ requires C, 58.66; H, 12.03; N, 7.60.

Bis(2-ethylhexyl)dimethylammonium isonicotinate, [BEDMA][Isonic]

Bis(2-ethylhexyl)dimethylammonium isonicotinate was prepared by the procedure described for [BEDMA][CH_3COO] from bis(2-ethylhexyl)dimethylammonium 4-*tert*-butylphenolate (15 g, 35.74 mmol**)** and isonicotinic acid (5.49 g, 44.68 mmol), to give a colourless solid. Yield: (11.50 g, 82%). mp: 266 ºC. ^{1}H NMR (300 MHz, D_2O): δ = 0.82 (m, 12H), 1.27 (m, 12H), 1.85 (m, 2H), 3.01 (s, 6H), 3.19 (m, 4H),7.69 (d, 2H, 6.33 Hz), 8.55 (d, 2H, 6.33Hz). **^{13}C** NMR (75MHz, D_2O): δ = 9.50, 13.26, 22.15, 25.79, 27.68, 32.35, 32. 41, 55.41, 70.27, 124.24, 146.15, 148.76, 171.66. Elemental analysis: Found: C, 70.26; H, 11. 32; N, 6.75. $C_{24}H_{44}N_2O_2{\cdot}H_2O$ requires C: 70.20, H: 11.29, N: 6.82%.

Bis(2-ethylhexyl)dimethylammonium nicotinate, [BEDMA][Nic]

Bis(2-ethylhexyl)dimethylammonium nicotinate was prepared by the procedure described for [BEDMA][CH_3COO] from bis(2-ethylhexyl)dimethylammonium 4-*tert*-butylphenolate (15 g,

35.74 mmol**)** and nicotinic acid (3.96 g, 32.16 mmol), to give a colourless solid .Yield: (11.22 g, 80%). mp: 224 ºC. ^{1}H NMR (300 MHz, D_2O): δ= 0.77 (m, 12H), 1.26 (m, 16H), 1.70 (m, 2H), 2.96 (s, 6H), 3.15 (m, 4H), 7.38 (m, 1H), 8.20 (d, 1H, 7.98 Hz), 8.48 (d, 1H, 7.14 Hz), 8.92 (s, 1H). ^{13}C NMR (75 MHz**,** D_2O): δ = 9.50, 13.31, 22.14, 25.70, 27.65, 32.29, 33.27, 49.81, 70.07, 125.82, 134.42, 142.89, 144.76, 145.57, 169.53. Elemental analysis: Found: C, 67.15; H, 11. 10; N, 6.60. $C_{24}H_{44}N_2O_2{\cdot}2H_2O$ requires C, 67.25; H, 11.29; N, 6.54%.

Bis(2-ethylhexyl)dimethylammonium picolinate, [BEDMA][Pic]

Bis(2-ethylhexyl)dimethylammonium picolinate was prepared by the procedure described for [BEDMA][CH_3COO] from bis(2-ethylhexyl)dimethylammonium 4-*tert*-butylphenolate (15 g, 35.74 mmol**)** and picolinic acid (4.39 g, 35.74 mmol), to give a colourless liquid. Yield: (11.92 g, 85%). ^{1}H NMR (300 MHz, D_2O): δ = 0.77 (m, 12H), 1.22 (m, 16H), 1.79 (m, 2H), 2.95 (s, 6H), 3.13 (m, 4H), 7.81 (m, 1H), 8.13 (d, 1H, 7.88Hz), 8.31 (m, 1H), 8.60 (d, 1H, 5.07 Hz). ^{13}C NMR (75MHz, D_2O): δ= 9.53, 13.26, 22.15, 25.82, 27.68, 32.35, 33.30, 49.60, 55.40, 70.26, 125.53, 127.31, 143.43, 144.29, 148.19, 166.81. Elemental analysis: Found: C, 63.51; H, 23.28; N, 6.11. $C_{24}H_{44}N_2O_2{\cdot}3H_2O$ requires: C, 63.62; H, 23.14; N, 6.18%.

Results and Discussion

The bis(2-ethylhexyl)dimethylammonium cation $[BEDMA]^+$ was selected as cation for the base stable ionic liquids, because it is accessible via the secondary amine bis(2-ethylhexyl)amine, which is a widely available and cheap starting material. The 2-ethylhexyl group is an often used branched alkyl chain, since it is prepared from butyraldehyde, a product of the hydroformylation of propene. In the past, [BEDMA][Cl] has been used as an anionic extractant for the liquid-liquid extraction of cobalt(II), iron(III), indium(III) and

gallium(III) from chloride medium.[39] However, the base stability of ionic liquids based on the $[BEDMA]^+$ cation has never been investigated.

The synthesis of the ionic liquids consists of the following steps: (1) quaternization of the secondary amine bis(2-ethylhexyl)amine by dimethyl sulfate; (2) transformation of the dimethyl sulphate salt into the corresponding 4-*tert*-butylphenolate salt; (3) reaction of the 4-*tert*-butylphenolate salt with a Brønsted acid (Scheme 1). The synthetic route was based on the so-called "phenolate platform", that we have introduced recently.[40] It must be noted that the ionic liquids were prepared via a halogen-free route, and that no detectable amounts of halide are present, with the exception, of course, of the chloride, bromide and iodide salts. The quaternization of bis(2-ethylhexyl)amine was performed by the reaction with two equivalents of dimethyl sulfate, in acetonitrile, in the presence of potassium carbonate. After 48 hours of heating under reflux, complete conversion of the starting amine was achieved. The precipitated potassium salts were removed by filtration and the solvent was removed *in vacuo*. The dimethyl sulphate salt $[BEDMA][CH_3OSO_3]$ was obtained as a highly viscous pale yellow liquid in very good yield (96%). The product was characterized by ^1H NMR, ^{13}C NMR spectroscopy and CHN elemental analysis. Attempts to introduce alkyl groups other than a methyl group, such as an ethyl or a butyl group, were not successful, probably because of the steric hindrance by the ethyl group in the 2-position of bis(2-ethylhexyl)amine. It has been tried to react bis(2-ethylhexyl)amine with 1-bromoethane, 1-bromopropane and 1-iodobutane. In all the cases, the unreacted starting materials were recovered after the reaction. No evidence for formation of tertiary amines were observed in the reaction mixture.

The second step was the synthesis of the phenolate precursor, from which the desired anions were introduced by ion-exchange reactions with Brønsted acids. This was achieved by the extraction of the $[BEDMA]^+$ cation from the aqueous phase to the organic phase by stirring with sodium 4-*tert*-butylphenolate. The phenolate precursor ionic liquid,

[BEDMA][4-*tert*-butylphenolate] was obtained as a highly viscous liquid with 85 % yield. Sodium 4-*tert*-butylphenolate was prepared by the reaction of 4-*tert*-butylphenol and sodium hydroxide in ethanol. Initially, we tried to use sodium phenolate instead of sodium 4-*tert*-butylphenolate for the extraction of the $[BEDMA]^+$ cation from the aqueous phase to the organic phase. The intent was to remove the phenol that was formed after the ion-exchange reaction with Brønsted acids *in vacuo*. Even though extraction of $[BEDMA]^+$ was achieved, the complete removal of phenol from the ionic liquid formed after the ion-exchange reaction with Brønsted acids was not successful. The third step was the introduction of different anions by ion exchange of the [BEDMA][4-*tert*-butylphenolate] with different Brønsted acids to obtain the desired ionic liquids. The following Brønsted acids were used: formic acid, acetic acid, propionic acid, trifluoroacetic acid, methanesulfonic acid, para-toluenesulfonic acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, nitric acid, sulphuric acid, phosphoric acid, nicotinic acid, isonicotinic acid and picolinic acid. Ion-exchange reaction was carried out by adding an aqueous solution of Brønsted acid to a solution of [BEDMA][4-*tert*-butylphenolate] in toluene. The reaction mixture was vigorously stirred for 30 minutes. The ionic liquid formed was transferred to the aqueous layer because of its overall hydrophilic nature. The side product of the ion exchange reaction was 4-*tert*-butylphenol, which stayed in the organic layer. The hydrophilic ionic liquid was isolated by separation of the aqueous layer from the organic phase and the evaporation of water under reduced pressure. The ^{1}H NMR spectra showed the complete disappearance of the phenolate anion from the final ionic liquids. Due to the hydrophobic nature of the 4-*tert*-butylphenol, the side product of the ion-exchange reaction, it does not contaminate the hydrophilic ionic liquids formed. It was possible to recover 4-*tert*-butylphenol after the ion exchange reaction and it could be reused for the preparation of sodium-4-*tert*-butylphenolate for the next stage. The ion-exchange reaction is preferably performed in a non-polar organic solvent to avoid the reduction in the

yield of the final ionic liquids. Ion-exchange reactions in polar solvents lead to lower yields, which are caused by the solubility of these ionic liquids in polar solvents, i.e. a major portion of the ionic liquids formed during the ion exchange reaction would stay in the organic phase together with the 4-*tert*-butylphenol. A higher or lower relative integration of the protons of the anions was observed in the ^{1}H NMR spectra when stoichiometric amounts of Brønsted acids were used for the ion-exchange reaction. To obtain a perfect 1:1 ratio between cation and anion, the amount of Brønsted acid used had to be tuned for every specific acid. Ion-exchange reactions were carried out in other non-polar solvents to study the efficiency of the process in other solvent systems. Different solvents such as cyclohexane, *m*-xylene, *tert*-butyl methyl ether, *n*-heptane were used for the ion-exchange reaction. There was not a considerable variation in the yields when different non-polar solvents were used. Hence, different non-polar solvents, which are immiscible with water, can be used for the ion-exchange reaction.

[Insert Scheme 1]

The chloride, bromide, iodide, nitrate and tosylate salts are solids at room temperature with a melting point between 73 °C and 90 °C (Table 1). An interesting behavior is observed for the pyridinecarboxylates. The nicotinate (mp: 224 °C) and the isonicotinate (mp: 266 °C) are high-melting solids, whereas the isomer with the picolinate anion is a room-temperature ionic liquid. This large difference in the melting point may be due to the asymmetry in the anion, or differences in the interactions between cations and anions (for instance, hydrogen bonding). More studies are needed to explain this observation, but no single crystals of a quality high enough for X-ray diffraction could be obtained. All the other compounds were liquid at room temperature. The densities, viscosities and residual water content of the ionic

liquids were measured (Table 2). By drying of the ionic liquids in high vacuum (10^{-2} to 10^{-3} mbar) for 48 hours at 75 ° C, the water content was reduced to less than about 1000 ppm (determined by coulometric Karl Fischer titration). The viscosities of the ionic liquids were measured at 25 °C. The viscosities are high, and are ranging between 1450 cP and 4700 cP. All the ionic liquids with the bis(2-ethylhexyl)dimethylammonium cation are completely miscible with water, ethanol, DMSO, dichloromethane and chloroform. They form a biphasic mixture with diethylether and toluene. The miscibility tests were performed at room temperature and the ionic liquid to solvent volume ratio was about 1:1.

The base stability of the $[BEDMA]^+$ cation was studied using ^1H NMR spectroscopy. In a typical experiment, the reaction flask was thermostated at a selected temperature between room temperature and 80 °C and charged with 20 mL of 1,2-dichloroethane solution of [BEDMA][Cl] (3.26 mmol) and 20 mL of a 50 wt% NaOH solution. Stirring and time logging were started. Samples of (1-2 mL) of organic phase were withdrawn at various times by stopping the stirrer for 40 to 60 seconds to allow adequate separation. The organic layer was evaporated and ^1H NMR spectra of the sample were recorded. The possible Hofmann degradation products of the $[BEDMA]^+$ cation are 2-ethyl-hex-1-ene and 2-ethyl-*N*,*N*-dimethylhexan-1-amine. Even after a long reaction time (120 hours), no evidence for the decomposition of the starting material was observed at room temperature. Similar results were obtained when the reactions were conducted at higher temperatures, i.e. at 40 °C, 60 °C and 80 °C. The ^1H NMR spectra contained only the peaks of the starting material. These results indicate that the $[BEDMA]^+$ cation is very stable against strong bases at elevated temperatures. This is the more remarkable when this stability is compared with that of other quaternary ammonium salts. Landini *et al.* carried out a systematic study on the stability of a series of quaternary ammonium salts in aqueous /organic systems in the presence of an aqueous alkaline solution as a function of alkyl chain length.[37] For instance, 50% of

tetrahexylammonium chloride was found to be decomposed after 35 hours at 25 °C. When the temperature was raised to 60 °C, the half-life time dropped to 0.4 hours. The higher base stability of $[BEDMA]^+$ ionic liquids can be explained by the steric hindrance caused by the branching, which limits the accessibility of the β-hydrogen by the base.

[Insert Table 1]

[Insert Table 2]

Conclusions

A range of ionic liquids based on the bis(2-ethylhexyl)dimethylammonium cation, $[BEDMA]^+$, were prepared by a halide-free route starting from the readily available secondary amine bis(2-ethylhexyl)amine. Most of the ionic liquids prepared are liquid at room temperature. The ^{1}H NMR studies showed that this new class of ionic liquids is very stable under strongly alkaline conditions. The ionic liquids are completely miscible with water and polar organic solvents, but form a biphasic mixture with diethylether and toluene.

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Electronic supporting information

Electronic supplementary information (ESI) available: copies of the ^{1}H NMR and ^{13}C NMR spectra of all ionic liquids.

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Figure caption

Scheme 1. Three-step procedure for the synthesis of ionic liquids derived from the bis(2-ethylhexyl)dimethylammonium cation, $[BEDMA]^+$.

Scheme 1.

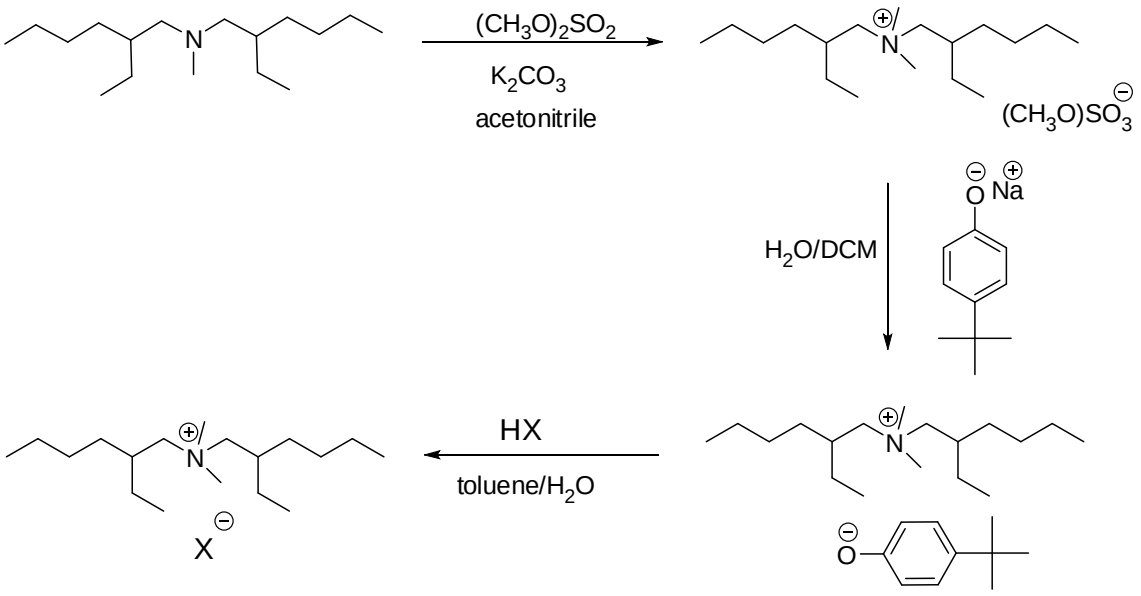
(CH3O)2SO2
K2CO3
acetonitrile
(CH3O)SO3
H2O/DCM
Na
HX
toluene/H2O
X

Table 1. Melting points (T_m) of ionic liquids.

Compound[a],[b]	T_m (°C)[c]
[BEDMA][Cl]	84
[BEDMA][Br]	90
[BEDMA][I]	73
[BEDMA][NO_3]	80
[BEDMA][TsO]	78
[BEDMA][Isonic]	266
[BEDMA][Nic]	224

[a] Abbreviations: TsO = tosylate, Isonic = isonicotinate, Nic = nicotinate. [b] All other ionic liquids were liquid at room temperature (see Table 2).

[c] The melting point was determined by DSC.

Table 2. Physicochemical properties of the room temperature ionic liquids.

Compound[a],[b]	Density ($g\ cm^{-3}$) [c]	Viscosity (cP) [d]	Water Content (ppm) [e]
[BEDMA][CH_3COO]	0.98	1445	610
[BEDMA][CH_3CH_2COO]	1.01	2500	720
[BEDMA][CF_3COO]	0.90	1500	810
[BEDMA][HCOO]	0.91	2600	670
[BEDMA][CH_3SO_3]	0.96	2850	760
[BEDMA][Pic]	1.22	n.d.	780
[BEDMA][HSO_4]	1.29	4500	780

[a] (All the other ionic liquids are solids (see Table 1). [b] Abbreviation: Pic = picolinate (pyridine-2-carboxylic acid); [c] Density measured at 19 °C. [d] Viscosity measured at 25 °C, n.d.: not determined, due to experimental difficulties (viscosity too high). [e] Measured by coulometric Karl Fischer titration.